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## Synthesis, characterization and applications of Organomercury(II) pyrrolidine-N-thiohydrazide complexes

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The complexes of organomercury(II) with pyrrolidine-N-thiohydrazide of the type  $RHg(L)Cl$  where  $R=C_6H_5$  (phenyl),  $p-ClC_6H_4$  (p-chlorophenyl),  $p-BrC_6H_4$  (p-bromophenyl),  $o-$ ,  $p-HOC_6H_4$  (o-, p-hydroxyphenyl),  $L$  = pyrrolidine-N-thiohydrazide, have been synthesized and characterized by elemental analysis, IR,  $^1H$ -NMR and electronic spectral analysis. Thermogravimetric and differential thermal analytical curves are used to calculate thermodynamic parameters and variations in these parameters have been correlated with complex structural parameters. All complexes were tested in vitro for their antibacterial activity against Gram-negative bacteria, namely, *Escherichia coli*, *Zymomonas mobilis* and against two pathogenic fungal strains, namely, *Aspergillus niger* and *Cerveleria*.

**Keywords:** Apparent activation energy; Heat of reaction; Antibacterial activity, Organomercury(II) complexes

Thiohydrazides are the hydrazine derivatives of dithioacid ( $RCS_2H^+$ ). Many workers<sup>1-5</sup> prepared and characterized thiohydrazide complexes with various metals. Thiohydrazides can exhibit thione-thiol tautomerism and form a five-membered chelate ring by coordinating as bidentate N-S chelation. Some papers on the mercury complexes of substituted thiohydrazides have been published<sup>6,7</sup>. In a series of these applications of thiohydrazides<sup>8-12</sup>, this work has been designed to prepare organomercury complexes of thiohydrazides.

### Materials and Methods

All the reagents of AR grade, viz., mercury (Merck), pyrrolidine (Merck) and hydrazine hydrate (Central Drug House, India) were used as received. All the chemicals and solvents used were dried and purified by standard methods<sup>13</sup> and all the glass apparatus were dried by keeping in an oven at 200 °C. The melting points were recorded in open capillaries with electronic melting point apparatus. C, H, and N analysis were done at RSIC, Punjab University, Chandigarh. The amount of sulphur was estimated gravimetrically as barium sulfate ( $BaSO_4$ ), chlorine and mercury were estimated gravimetrically as silver chloride and mercuric sulfide<sup>13</sup>. Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer was used to

record IR and far IR. spectra. Beckman DU-64, UV-visible spectrophotometer was used to record electronic spectra. Elico Conductivity Bridge Model CM – 102, India was used to measure conductance. The  $^1H$ -NMR spectra were recorded at room temperature on Hitachi R-600 FT-NMR spectrometer at a spectral width of 60 MHz and Bruker spectropin advance 300 spectrometer at a spectral width of 300 MHz. Perkin-Elmer, model TGA-7, USA was used to record Thermogravimetric (TG) curves in static air. Rigaku model 8150 thermoanalyzer was used to record differential thermal analytical (DTA) curves in static air at a heating rate of 10 °C min<sup>-1</sup>. The agar well diffusion method<sup>14</sup> was used to evaluate bactericidal activities while Czapek Dox nutrient medium<sup>15</sup> was used to culture fungi.

### Antibacterial activity

The media was prepared as per the guidelines given in the Bacteriology Manual<sup>14</sup>. All the dry ingredients given in the manual were taken in a beaker and dissolved in distilled water. The prepared medium was sterilized by keeping this in an autoclave at 121 °C for 30 min. Antibacterial activities of all the complexes were tested by agar well diffusion method against Gram-negative bacteria, namely, *Escherichia coli*, *Zymomonas mobilis*, prepared by the standard

process. Before the use, Petri plates and media were autoclaved. 15 mL of media was uniformly spread in each Petri plate. All the bacterial cultures were compared to a bacterial suspension of approximately  $1.5 \times 10^8$  CFU/mL. 100  $\mu$ L inoculum of test micro-organisms was swabbed in each Petri plate. With the help of a cork borer of 8 mm diameter, wells were bored in each Petri plate. These wells were loaded with 100  $\mu$ L of organomercury complex dissolved in Dimethyl sulfoxide (DMSO) at concentration 25, 50, and 100  $\mu$ g/mL. The central hole of all the Petri plates was filled with DMSO (control). Then all the Petri plates were kept in an incubator maintained at 37 °C for 24 h. The zone of inhibition formed was measured and compared with that of the DMSO to evaluate the zone of inhibition due to the complexes.

#### Antifungal activity

The antifungal activities of all the complexes were evaluated against *Aspergillus niger* and *Cerveleria* using Czapek Dox Nutrient medium<sup>15</sup>. 15 mL of inoculated media was uniformly spread in each Petri plate. With the help of a cork borer of 8 mm diameter, wells were bored in each Petri plate. These wells were loaded with 100  $\mu$ L of organomercury complex dissolved in DMSO at concentrations 25, 50, and 100  $\mu$ g/mL. The central hole of all the Petri plates was filled with DMSO (control). Then all the Petri plates were kept in an incubator maintained at 25 °C for 7 days. The zone of inhibition formed was measured and compared with that of the DMSO to evaluate the zone of inhibition due to the complexes.

#### Synthesis of pyrrolidine-N-thiohydrazides

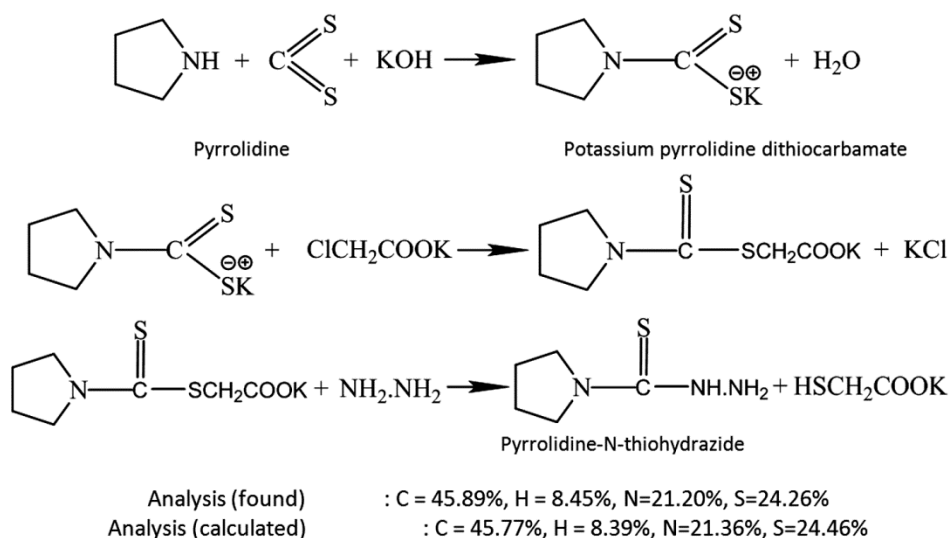
Pyrrolidine-N-thiohydrazide was prepared by modified literature method<sup>16-19</sup>. The piperidine (0.4 moles) was dissolved in methanol, chilled and with constant stirring, potassium hydroxide (0.4 moles) in aqueous methanol was added to it. Carbon disulfide (0.4 moles) in methanol solution was then added slowly to the mixture, keeping the temperature below 10 °C. A white color crystalline precipitate of the potassium salt of pyrrolidine dithiocarbamate obtained but it soon disappeared due to its high solubility in aqueous methanol. So, to proceed further a solution of the freshly prepared potassium salt of monochloroacetate (0.4 moles) was added to the same reaction mixture. The reaction mixture temperature first increased and after that maintained below 40 °C for 1 h. The reaction mixture was then allowed to stand for 24 h at room temperature. After 24 h the methanol solution of 98% hydrazine hydrate (0.4 moles) was added, this reaction mixture was heated for 2 h on a water bath, by doing so the desired product was separated. This product was cooled in an ice bath for 15 h and then filtered. So obtained thiohydrazide was dried and recrystallized. The reaction proceeds in the manner as shown Scheme 1.

#### Synthesis of Organomercury compound

Organomercury compounds were prepared by literature method<sup>20</sup>.

#### Phenyl Mercuric Chloride

24 g of mercuric oxide was added at 50 °C with stirring to 102 ml acetic acid and a solution of 800 mg



Scheme 1 — Synthesis of pyrrolidine-N-thiohydrazide

boron trifluoride ( $\text{BF}_3$ ) in 4 mL acetic acid in a round bottom flask. To the clear solution so obtained, 100 mL of benzene was added and the contents were refluxed for about 24 h. The reaction mixture was concentrated under vacuum to about 50 mL and added to a hot solution of sodium chloride (50 g in 250 mL of water). It was cooled to room temp, filtered and washed several times with hot water and finally dried. The yield was 57% and m.p. of this compound was found 255 °C.

#### *o*- and *p*-hydroxyphenylmercuric chloride

12 g of phenol was heated in a water bath and it added 25 g of mercuric acetate gradually with constant stirring. After that added boiling water, when acetate was dissolved completely and boiling of the mixture was continued for 10 min. A hot solution of 5 g sodium chloride in 25 mL water was added. The precipitate of *p*-hydroxyphenylmercuric chloride was separated and then filtered while hot. When the filtrate was allowed to stand, the crystals of *o*-hydroxyphenyl mercuric chloride deposited. The *p*-hydroxyphenyl mercuric chloride was repeatedly washed with hot water while the *o*-hydroxyphenylmercuric chloride was recrystallized from boiling water. The obtained yield of *o*- $\text{OHC}_6\text{H}_4\text{HgCl}$  and *p*- $\text{OHC}_6\text{H}_4\text{HgCl}$  was 30% and 50%, respectively. The melting point was found 151 °C for *o*- $\text{OHC}_6\text{H}_4\text{HgCl}$  and 226 °C for *p*- $\text{OHC}_6\text{H}_4\text{HgCl}$ .

#### *p*-chloro and *p*-bromophenylmercuric chloride

The mercuric acetate (8.0 g) was added to the boiling chlorobenzene and bromobenzene (20 mL) respectively and the solution was refluxed for 5 h. The clear hot solution was then poured into a boiling aqueous solution of sodium chloride (100 mL, 20%) when a white precipitate separated immediately. It was cooled, filtered and washed with water and dried. The obtained yield of *p*- $\text{ClC}_6\text{H}_4\text{HgCl}$  and *p*- $\text{BrC}_6\text{H}_4\text{HgCl}$  was 70% and 67%, respectively. The melting point was found 215 °C for *p*- $\text{BrC}_6\text{H}_4\text{HgCl}$  and 209 °C for *p*- $\text{ClC}_6\text{H}_4\text{HgCl}$ . The synthesis of organomercury chlorides can be shown by Scheme 2.

#### Synthesis of Thiohydrazide complexes

A solution of pyrrolidine thiohydrazide (L, 3.18 g, 0.02 mole) in 25 mL tetrahydrofuran (THF) was added slowly to a solution of  $\text{RHgCl}$  (0.02 mole) in 25 mL THF. The contents were stirred for about 7 h at room temperature and reflux for 5 h. The resulting solids were filtered, washed with water and then dried

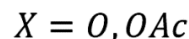
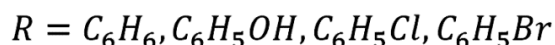
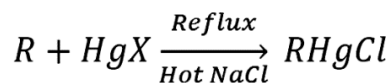
in vacuum. This synthesis can be represented by Scheme 3.

## Results and Discussion

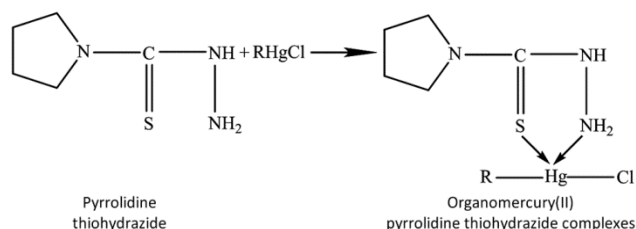
The thiohydrazides act as bidentate ligands in the Organomercury (II) complexes  $[\text{RHg}(\text{L})\text{Cl}]$  coordination being through the thiol sulfur and terminal nitrogen. The complexes were of good purity as revealed from satisfactory elemental analysis and spectral analysis for the ligand and synthesized complexes, given in the Table 1. The complexes obtained were powdered and colourless. These compounds are non-electrolyte as indicated by the conductance of these complexes i.e.  $< 10 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$ . All the attempts to recrystallize organomercury (II) complexes were unsuccessful because of the solubility of these complexes as they are insoluble in most of the organic solvents and soluble in DMSO only.

#### UV absorption spectra

Thiohydrazides show high – intensity absorption in the ultraviolet region. These absorptions are due to the chromophore  $\text{N}=\text{C}=\text{S}$  group. One absorption band  $\sim 290 \text{ nm}$  is observed which is assigned to a  $\pi - \pi^*$  electronic transition. Pyrrolidine -N-thiohydrazide (L) absorbs at 297 nm.  $\text{C}=\text{S}$  group is involved in complexation as clear from the blue shifting of this band in complexes. Because of metal-ligand charge transfer, one additional band also appears in the complexes. The electronic spectral data of thiohydrazide complexes is presented in Table 2.



Scheme 2 — Synthesis of Organomercury Chlorides



Scheme 3 — Synthesis of Thiohydrazide Complexes

**IR spectra**

In the IR spectra, the  $\nu(\text{N-H})$  band at  $3200\text{--}2930\text{ cm}^{-1}$  is shifted towards higher frequency, suggesting the involvement of terminal ( $\text{NH}_2$ ) nitrogen in bonding to the metal atom. A sharp and strong band at  $\sim 885\text{ cm}^{-1}$  in IR spectra of a ligand which is shifted in complexes is credited to thioamide band IV due to  $\nu(\text{C}=\text{S})$ . This shifting suggests the bonding of the thioamide group through sulfur to the metal atom. The four important IR bands,  $\nu(\text{C}=\text{S})$ ,  $\nu(\text{N-H})$ ,  $\nu(\text{C-N})$  and  $\nu(\text{C}=\text{N})$  are because of the thioamide group. On complex formation, all these IR bands are shifted because the

bond character of the  $\text{C-N}$  group increased on complexation. This shows that coordination to a metal ion is through the thioamide sulfur  $\text{C}=\text{S}$ . Hence, the spectra indicates bidentate coordination mode of the ligands via sulfur and terminal nitrogen in thiohydrazide complexes. In the complexes the metal nitrogen vibrations,  $\nu(\text{M-N})$  are assigned to new bands<sup>19</sup> in the far IR spectrum in the  $690\text{--}600\text{ cm}^{-1}$  region, while the  $365\text{--}350\text{ cm}^{-1}$  region corresponds to metal-sulfur band stretching<sup>21</sup>. The band at  $380\text{--}370\text{ cm}^{-1}$  is due to the metal chlorine stretching vibration mode. The IR spectral data of thiohydrazide complexes is presented in Table 3.

Table 1 — Elemental analysis of Thiohydrazide complexes

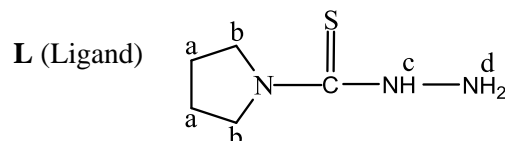
Complexes	Found (Calculated) %					
	C	H	N	S	Cl	Metal
p-Cl $\text{C}_6\text{H}_4\text{Hg}(\text{L})\text{Cl}$	26.95 (26.77)	3.43 (3.04)	8.24 (8.51)	6.67 (6.50)	14.25 (14.19)	40.81 (40.70)
p-Br $\text{C}_6\text{H}_4\text{Hg}(\text{L})\text{Cl}$	24.41 (24.57)	2.62 (2.79)	7.94 (7.82)	6.04 (5.97)	6.72 (6.61)	37.65 (37.36)
p-OH $\text{C}_6\text{H}_4\text{Hg}(\text{L})\text{Cl}$	28.05 (27.83)	3.46 (3.37)	8.61 (8.85)	6.89 (6.77)	7.41 (7.48)	42.45 (42.32)
o-OH $\text{C}_6\text{H}_4\text{Hg}(\text{L})\text{Cl}$	27.62 (27.83)	3.01 (3.37)	8.76 (8.85)	6.25 (6.77)	7.16 (7.48)	42.10 (42.32)
$\text{C}_6\text{H}_5\text{Hg}(\text{L})\text{Cl}$	28.51 (28.81)	3.65 (3.49)	9.25 (9.16)	6.72 (6.99)	7.42 (7.74)	43.51 (43.78)

Table 2 — Electronic spectral data of Thiohydrazide Complexes

Complexes	$\lambda_{\text{max}}$ (nm)	$\log(\epsilon)$
p-Cl $\text{C}_6\text{H}_4\text{Hg}(\text{L})\text{Cl}$	300 352	2.126 2.132
p-Br $\text{C}_6\text{H}_4\text{Hg}(\text{L})\text{Cl}$	299 351	2.072 2.040
p-OH $\text{C}_6\text{H}_4\text{Hg}(\text{L})\text{Cl}$	300 352	1.697 1.632
o-OH $\text{C}_6\text{H}_4\text{Hg}(\text{L})\text{Cl}$	304 354	1.657 1.614
$\text{C}_6\text{H}_5\text{Hg}(\text{L})\text{Cl}$	299 347	2.065 2.012

 **$^1\text{H-NMR}$** 

$d_6$ -DMSO was used to record  $^1\text{H-NMR}$  spectra of the complexes taking TMS as the internal standard. As a result of the coordination of the ligand to a metal ion, a downfield shift in the position of resonance signals of the complexes in comparison to the free ligands was observed. No trace of the free ligands was noticed which shows that complexes do not dissociate on dissolution.



**L** :  $\delta$  (ppm) 1.9-2.0(m,  $4\text{H}^a$ , -  $\text{CH}_2$ ), 3.0-3.3(t,  $4\text{H}^b$ , -  $\text{CH}_2$ ), 8.9(S, br,  $1\text{H}^c$ , -NH), 3.6(S, br,  $2\text{H}^d$ , - $\text{NH}_2$ )

**p-Cl  $\text{C}_6\text{H}_4\text{Hg}(\text{L})\text{Cl}$**  :  $\delta$  (ppm) 7.5-7.8(m,  $4\text{H}$ , Ar-H), 2.3-2.4(m,  $4\text{H}^a$ , -  $\text{CH}_2$ ), 3.5-3.7(t,  $4\text{H}^b$ , - $\text{CH}_2$ ), 9.3(S, br,  $1\text{H}^c$ , -NH), 3.9(S, br,  $2\text{H}^d$ , - $\text{NH}_2$ )

**p-Br  $\text{C}_6\text{H}_4\text{Hg}(\text{L})\text{Cl}$**  :  $\delta$  (ppm) 7.0-7.4(m,  $4\text{H}$ , Ar-H), 2.2-2.4(m,  $4\text{H}^a$ , -  $\text{CH}_2$ ), 3.6-3.8(t,  $4\text{H}^b$ , - $\text{CH}_2$ ), 9.25(S, br,  $1\text{H}^c$ , -NH), 4.1(S, br,  $2\text{H}^d$ , - $\text{NH}_2$ )

**p-OH  $\text{C}_6\text{H}_4\text{Hg}(\text{L})\text{Cl}$**  :  $\delta$  (ppm) 7.7-7.9(m,  $4\text{H}$ , Ar-H), 2.4-2.5(m,  $4\text{H}^a$ , -  $\text{CH}_2$ ), 3.5-3.7(t,  $4\text{H}^b$ , - $\text{CH}_2$ ), 9.5(S, br,  $1\text{H}^c$ , -NH), 4.0(S, br,  $2\text{H}^d$ , - $\text{NH}_2$ )

Table 3 — IR spectral data of Thiohydrazide complexes

Complexes	$\nu(\text{N-H})$	$\nu(\text{CN})^+$ $\delta(\text{NH})$	$\nu(\text{NH})$ $+\nu(\text{CN})$	$\nu(\text{NN})$	$\nu(\text{C=S})$	$\nu(\text{M-N})$	$\nu(\text{M-S})$	$\nu(\text{M-Cl})$
L	3135,2950	1500	1340	1027	870	-	-	-
p-Cl $\text{C}_6\text{H}_4\text{Hg}(\text{L})\text{Cl}$	3199,2999	1580	1350	1030	834	676	360	377
p-Br $\text{C}_6\text{H}_4\text{Hg}(\text{L})\text{Cl}$	3151,2976	1576	1330	1025	832	676	361	370
p-OH $\text{C}_6\text{H}_4\text{Hg}(\text{L})\text{Cl}$	3155,2980	1575	1352	1023	830	675	355	380
o-OH $\text{C}_6\text{H}_4\text{Hg}(\text{L})\text{Cl}$	3172,2997	1570	1347	1032	830	670	359	376
$\text{C}_6\text{H}_5\text{Hg}(\text{L})\text{Cl}$	3182,3000	1570	1349	1032	830	670	360	377

**o-OHC<sub>6</sub>H<sub>4</sub>Hg(L)Cl** :  $\delta$  (ppm) 7.2-7.6(m, 4H, Ar-H), 2.3-2.6(m, 4H<sup>a</sup>, -CH<sub>2</sub>), 3.7-3.9(t, 4H<sup>b</sup>, -CH<sub>2</sub>), 9.42(S, br, 1H<sup>c</sup>, -NH), 4.21(S, br, 2H<sup>d</sup>, -NH<sub>2</sub>)

**C<sub>6</sub>H<sub>5</sub>Hg(L)Cl** :  $\delta$  (ppm) 7.7-7.9(m, 5H, Ar-H), 2.5-2.8(m, 4H<sup>a</sup>, -CH<sub>2</sub>), 3.7-3.8(t, 4H<sup>b</sup>, -CH<sub>2</sub>), 9.5(S, br, 1H<sup>c</sup>, -NH), 4.11(S, br, 2H<sup>d</sup>, -NH<sub>2</sub>)

**L** :  $\delta$  (ppm) 1.9-2.0(m, 4H<sup>a</sup>, -CH<sub>2</sub>), 3.0-3.3(t, 4H<sup>b</sup>, -CH<sub>2</sub>), 8.9(S, br, 1H<sup>c</sup>, -NH), 3.6(S, br, 2H<sup>d</sup>, -NH<sub>2</sub>)

**p-ClC<sub>6</sub>H<sub>4</sub>Hg(L)Cl** :  $\delta$  (ppm) 7.5-7.8(m, 4H, Ar-H), 2.3-2.4(m, 4H<sup>a</sup>, -CH<sub>2</sub>), 3.5-3.7(t, 4H<sup>b</sup>, -CH<sub>2</sub>), 9.3(S, br, 1H<sup>c</sup>, -NH), 3.9(S, br, 2H<sup>d</sup>, -NH<sub>2</sub>)

**p-BrC<sub>6</sub>H<sub>4</sub>Hg(L)Cl** :  $\delta$  (ppm) 7.0-7.4(m, 4H, Ar-H), 2.2-2.4(m, 4H<sup>a</sup>, -CH<sub>2</sub>), 3.6-3.8(t, 4H<sup>b</sup>, -CH<sub>2</sub>), 9.25(S, br, 1H<sup>c</sup>, -NH), 4.1(S, br, 2H<sup>d</sup>, -NH<sub>2</sub>)

**p-OHC<sub>6</sub>H<sub>4</sub>Hg(L)Cl** :  $\delta$  (ppm) 7.7-7.9(m, 4H, Ar-H), 2.4-2.5(m, 4H<sup>a</sup>, -CH<sub>2</sub>), 3.5-3.7(t, 4H<sup>b</sup>, -CH<sub>2</sub>), 9.5(S, br, 1H<sup>c</sup>, -NH), 4.0(S, br, 2H<sup>d</sup>, -NH<sub>2</sub>)

**o-OHC<sub>6</sub>H<sub>4</sub>Hg(L)Cl** :  $\delta$  (ppm) 7.2-7.6(m, 4H, Ar-H), 2.3-2.6(m, 4H<sup>a</sup>, -CH<sub>2</sub>), 3.7-3.9(t, 4H<sup>b</sup>, -CH<sub>2</sub>), 9.42(S, br, 1H<sup>c</sup>, -NH), 4.21(S, br, 2H<sup>d</sup>, -NH<sub>2</sub>)

**C<sub>6</sub>H<sub>5</sub>Hg(L)Cl** :  $\delta$  (ppm) 7.7-7.9(m, 5H, Ar-H), 2.5-2.8(m, 4H<sup>a</sup>, -CH<sub>2</sub>), 3.7-3.8(t, 4H<sup>b</sup>, -CH<sub>2</sub>), 9.5(S, br, 1H<sup>c</sup>, -NH), 4.11(S, br, 2H<sup>d</sup>, -NH<sub>2</sub>)

#### Thermal studies

The heat of reaction was derived from DTA curves. For some complexes, TG and DTA studies in a static air atmosphere have been carried out. TG and DTA curves are shown in Figs 1 and 2. Thermal data for the complexes are given in Table 4 and Table 5. Thermal studies were utilized to explain kinetic and thermodynamic parameters. TG curve indicates decomposition to be a single step process and the final residue weight corresponds to the metal oxide. The order of reaction for all the complexes is unity. The apparent activation entropies for all the complexes are positive. Hence these complexes show spontaneous thermal degradation. The activation energy ( $E_a$ ), apparent activation entropy ( $S^\ddagger$ ) and the order ( $n$ ) were calculated from TG curves by using Coats-Redfern method<sup>22</sup>. The plot is shown in Fig. 3.

Based on elemental analysis, spectral (UV, IR, and <sup>1</sup>H-NMR) data and thermal (TG/DTA) studies the following probable structure has been proposed for the complexes synthesized:

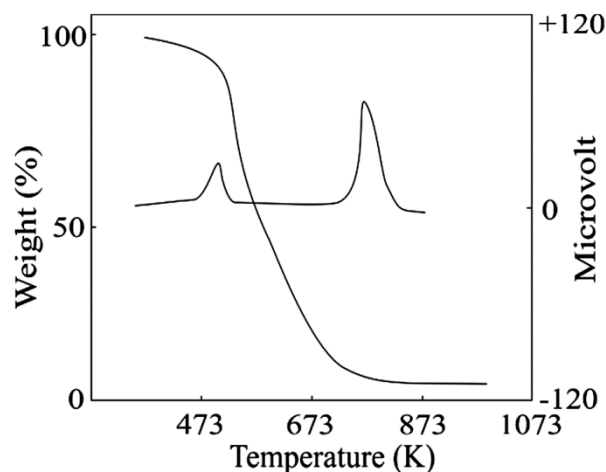
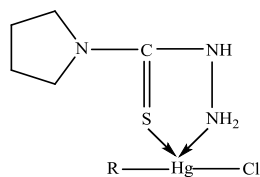


Fig. 1 — TG and DTA curves of p-BrC<sub>6</sub>H<sub>4</sub>Hg(L)Cl complex

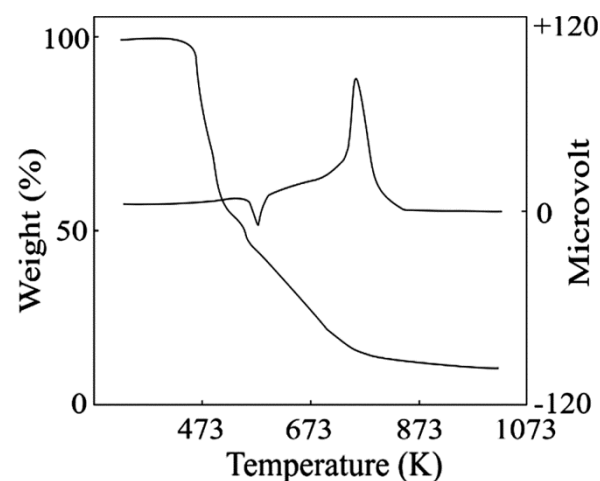


Fig. 2 — TG and DTA curves of p-ClC<sub>6</sub>H<sub>4</sub>Hg(L)Cl complex

Table 4 — Mass loss and thermal data for Thiohydrazide complexes

Complexes	Mass Loss		Thermogravimetry		
	Found (calc)%	Temp. range/K	n	$E_a$ (kJ mol <sup>-1</sup> )	$S^\ddagger$ (J K <sup>-1</sup> mol <sup>-1</sup> )
p-Cl C <sub>6</sub> H <sub>4</sub> Hg(L)Cl	54(56.07)	500-580	1	71.09	3.98
p-Br C <sub>6</sub> H <sub>4</sub> Hg(L)Cl	-	450-690	1	59.43	3.94
p-OHC <sub>6</sub> H <sub>4</sub> Hg(L)Cl	52(54.33)	430-585	1	54.61	4.01

Table 5 — Differential thermal data for Thiohydrazide complexes

Complexes	DTA		
	Thermal Effect	$T_{max}$ (K)	$\Delta H$ (J/g)
p-Cl C <sub>6</sub> H <sub>4</sub> Hg(L)Cl	Endothermic	610	22.00
	Exothermic	780	150.00
p-OHC <sub>6</sub> H <sub>4</sub> Hg(L)Cl	Exothermic	490	60.00
	Exothermic	785	117.00

Table 6 — Antibacterial activity of Thiohydrazide complexes (in mm)

Complexes	Z. mobilis			E. coli		
	25 µg/mL	50 µg/mL	100 µg/mL	25 µg/mL	50 µg/mL	100 µg/mL
p-Cl C <sub>6</sub> H <sub>4</sub> Hg(L)Cl	4	4	8	2	4	8
p-Br C <sub>6</sub> H <sub>4</sub> Hg(L)Cl	6	6	8	4	8	8
p-OHC <sub>6</sub> H <sub>4</sub> Hg(L)Cl	6	6	10	4	8	8
o-OHC <sub>6</sub> H <sub>4</sub> Hg(L)Cl	4	4	8	4	6	8
C <sub>6</sub> H <sub>5</sub> Hg(L)Cl	-	6	6	2	6	8

Table 7 — Antifungal Activity of Thiohydrazide Complexes

Complexes	A. niger			Cerveteria		
	25 µg/mL	50 µg/mL	100 µg/mL	25 µg/mL	50 µg/mL	100 µg/mL
p-Cl C <sub>6</sub> H <sub>4</sub> Hg(L)Cl	6	6	15	6	9	9
p-Br C <sub>6</sub> H <sub>4</sub> Hg(L)Cl	6	9	15	6	12	12
p-HOC <sub>6</sub> H <sub>4</sub> Hg(L)Cl	6	9	15	6	9	12
o-OH C <sub>6</sub> H <sub>4</sub> Hg(L)Cl	6	9	12	6	9	9

**Antimicrobial evaluation**

All the samples were tested against *E. coli*, *Z. mobilis* bacterial strains at three concentrations 25, 50 and 100 µg/mL. The order of activity against the two microorganisms is *Z. mobilis* > *E. coli*. The activities of the compounds against various microorganisms were measured in mm (diameter of the zones of inhibition). When there was no zone of inhibition the results have been indicated by (-) in Table 6.

All the complexes were tested for antifungal activity. The screening of all the samples was carried out against two fungal species, viz., *Aspergillus niger* and *Cerveteria* at three concentrations viz., 25, 50 and 100 µg/mL. When there was no zone of inhibition the results have been indicated by (-) in Table 7. The order of activity against the two fungi is *A. niger* > *Cerveteria*.

**Conclusions**

New Organomercury(II) pyrrolidine-N-thiohydrazide complexes were successfully synthesized and characterized. The activation energy, apparent activation entropy and the order were calculated from TG curves by using Coats-Redfern method<sup>22</sup>. All the samples were tested against bacterial strains and fungal species. The order of activity against the two microorganisms is *Z. mobilis* > *E. coli* and the order of activity against the two

fungi is *A. niger* > *Cerveteria*. It is observed that antimicrobial activities are concentration dependent as the conc. increases diameter of zone of inhibition also increase.

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